

## THERMOPHYSICAL PROPERTIES OF MATERIALS

# Attainable Superheating of Liquid Helium–Oxygen Solutions

V. G. Baidakov and A. M. Kaverin

*Institute of Thermophysics, Ural Division, Russian Academy of Sciences, Yekaterinburg, 620219 Russia*

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**Abstract**—The results are given of experimental investigations of the kinetics of nucleation in gas-saturated helium-oxygen solutions. The temperature dependences of the mean lifetime of solution in the metastable (superheated) state are determined for fixed values of pressure of 1.171 and 1.667 MPa and for several values of concentration. The experimental data are compared with the theory of homogeneous nucleation in a macroscopic approximation with due regard for the dependence of the properties of the nuclei on their size. The dimensional effect is included within van der Waals' gradient expansion. The problems associated with the construction of the kinetic theory of boiling of gas-saturated solutions are discussed, and good agreement is ascertained between the experimental data and the theory of nucleation when the latter includes the dimensional effect.

### INTRODUCTION

A supersaturated solution of gas in liquid is an example of a two-component metastable system in which the nonequilibrium is caused by the excess of the concentration of the dissolved (gas) component over the value of concentration in the saturated state. The supersaturation is removed as a result of isolation of the gas phase in the form of numerous bubbles ("champagne effect").

A special situation is observed for a gasified liquid at temperatures close to the critical point of the solvent. Here, a two-component system may prove to be "doubly" metastable. Given the temperature  $T$  and the concentration of dissolved component  $c'$ , a solution at a pressure  $p$  below the saturation pressure  $p_s$  is supersaturated and characterized by the degree of metastability  $\Delta p(T, c') = p_s - p$ , with the pure solvent being superheated by  $\Delta T(p) = T - T_s(c' = 0)$ , where  $T_s(c' = 0)$  is the saturation temperature of pure solvent at a given pressure.

Experimental investigations of limiting superheating  $\Delta T(p, c') = T - T_s$  of solutions of carbon dioxide and nitrogen in organic liquids at a low nucleation rate ( $J \approx 10^7 \text{ s}^{-1} \text{ m}^{-3}$ ) were performed by Mori *et al.* [1], by Forest and Ward [2], and, at a higher nucleation rate ( $J \approx 10^{24}–10^{26} \text{ s}^{-1} \text{ m}^{-3}$ ), by Skripov and Pavlov [3]. Mori *et al.* [1] and Forest and Ward [2] used the method of floating-up droplets, and Skripov and Pavlov [3] employed the method of pulsed heating of a wire probe. The gas saturation of liquid resulted in a shift of the boundary of spontaneous boiling towards lower temperatures. The authors of [1–3] observe an adequate agreement between the classical theory of homogeneous nucleation and the experimental data on the value of limiting superheating.

This study is aimed at determining the temperature, baric, and concentration dependences of the rate of

nucleation in gas-saturated solutions. The employed method of measuring the lifetime of metastable liquid enables one to determine the temperature of superheating the solution with an accuracy an order of magnitude higher than that of the methods used in [1–3]. The experiments are performed with solutions of helium in liquid oxygen. Gas-saturated solutions of cryogenic liquids belong to the class of weak solutions. At a pressure of 5 MPa, the solubility of helium in oxygen does not exceed 2–3 mol % [4]. A significant difference of the parameters of the potential of molecular interaction between the solvent and solute leads to a considerable nonideality of the two-component system; in this case, helium behaves as a surfactant and causes a decrease in the excess free energy of the liquid–vapor interface [5]. The simplicity of the molecular structure of solutions enables one to use van der Waals' theory of capillarity for including both the adsorption and dimensional effects in nucleation.

### EXPERIMENT

The experimental setup and procedure were described in [6]. A gas mixture of preassigned concentration was condensed into a measuring cell in the form of a glass capillary sealed on top and communicated with a metal sylphon bellows. The capillary was thermostatically controlled at a temperature  $T$ , and the temperature of the sylphon bellows was maintained close to that of normal boiling of oxygen. The supersaturation of the solution in the capillary was developed by releasing the pressure to a preassigned value of  $p$ . The concentration  $c'$  of the gas component in the liquid solution was determined by the data on phase equilibrium [4] using the method described in [6]. In the experiment, the time  $\tau$  from the moment of transformation of the solution to the metastable state to its boiling was measured for fixed values of  $T$ ,  $p$ , and  $c'$ . After boil-

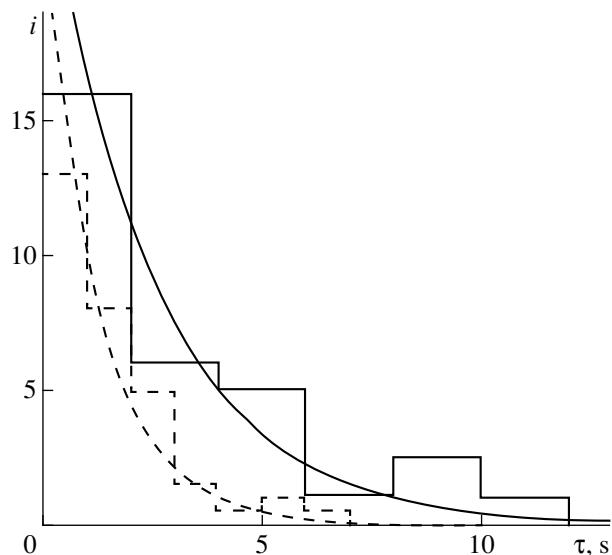
ing, the pressure in the system was increased to a value of  $p_b > p_s$ , where  $p_s$  is the saturation pressure. The solution was "held" in this state for some time  $\tau_b$ , after which the measurements were repeated. The mean time of waiting for boiling  $\tau = \sum_i \tau_i / N$  was found by the results of  $N = 20\text{--}100$  measurements. The error of determination of temperature was 0.05 K; that of pressure, 0.01 MPa; of time, 0.01 s; and of concentration, 0.02 mol %.

The experimentally recorded time  $\tau$  includes the time of waiting for the emergence of the first critical bubble,  $\tau_w$ , and the time  $\tau_g$  of its subsequent growth to a macroscopic size ( $\tau = \tau_w + \tau_g$ ). In the investigated range of parameters of state of helium-oxygen solutions,  $\tau_g \approx 10^{-3}$  s. The characteristic time of experiment is at least 0.1 s. The condition  $\tau \gg \tau_g$  enables one to assume  $\tau \approx \tau_w$  and calculate the nucleation rate as  $J = (\bar{\tau} V)^{-1}$ , where  $V = 68 \text{ mm}^3$  is the volume of metastable liquid.

The experiments were performed for two values of  $p = 1.171$  and  $1.667 \text{ MPa}$  and several values of concentration of helium in oxygen. The investigated substances were 99.99% (He) and 99.92% (O<sub>2</sub>) pure. The values of the mean lifetime of metastable solution being measured were in the range from 0.1 to 1000 s, this corresponding to the nucleation rate values of  $10^4\text{--}10^8 \text{ s}^{-1} \text{ m}^{-3}$ .

In the case of fixed external conditions ( $T, p, c' = \text{const}$ ), the emergence of the first viable nucleus in the metastable liquid is an event of the Poisson type [7]. A typical histogram of the experiments (the distribution of the number of boilings  $i$  falling within the interval of  $\tau, \tau + \Delta\tau$ ) is given in Fig. 1. The experiments revealed the dependence of the measurement result on the "hold" time  $\tau_b$ . For the values of time  $\tau_b \approx 3 \text{ min}$ , which are characteristic of experiments with one-component systems, boilings were often observed with the values of hold time that were "anomalously" small for the preassigned values of  $T, p$ , and  $c'$ . "Anomalously" small values of  $\tau$  could appear and disappear in the course of experiment or be retained throughout the measurements. This behavior of a gas-saturated system is analogous to that of a one-component system, when readily activated boiling centers are present in the latter [8]. The law of distribution of "anomalously" low values of the time of waiting for boiling is likewise close to Poisson's law (Fig. 1). When the "hold" time between measurements increases to 30–40 min (that is, by an order of magnitude!), no premature boiling of liquid was observed. In the course of processing of experimental data, the "anomalously" low values of  $\tau$  were eliminated from treatment.

Figure 2 gives, on a semilog scale, the temperature dependence of the nucleation rate in helium-oxygen at fixed values of pressure. The vertical dimension of the points corresponds to the statistical error of determination of  $J$ . As in the case of one-component liquids, two segments with different behavior of the temperature

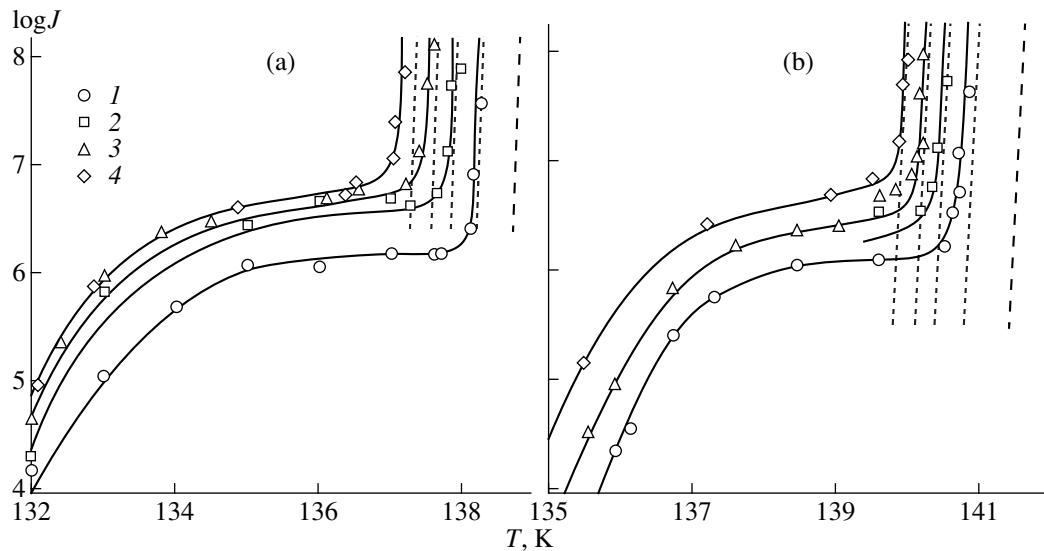


**Fig. 1.** A histogram of experiments ( $c' = 0.14 \text{ mol } \%$ ,  $p = 1.171 \text{ MPa}$ ,  $T = 166.66 \text{ K}$ ): Solid lines indicate  $N = 29$ ,  $\bar{\tau} = 2.66 \text{ s}$ , and  $\tau_b = 40 \text{ min}$ ; broken lines indicate  $N = 66$ ,  $\bar{\tau} = 1.34 \text{ s}$ , and  $\tau_b = 3 \text{ min}$ ; and smooth curves indicate the results of calculation by the exponential law.

dependence of the nucleation rate may be identified on the  $J(T)$  curves. In the case of low superheating, the experimental isobars have characteristic bends; as the temperature rises, these bends are replaced by segments with a sharp increase in the nucleation rate. The first segment is associated with initiated nucleation, and the second one is associated with spontaneous boiling of liquid solution. The dissolving of 0.1 mol % of helium in liquid oxygen causes an approximately 10% reduction of the limiting superheating  $\Delta T_{sh}(p, c') = T_{sh} - T_s$  in the region of spontaneous boiling of liquid. In so doing, the mean lifetime of solution in the region of initiated nucleation is reduced by a factor of three–four. Note that the gas saturation in this case shows up at very low concentrations of helium.

High-energy particles, generated by cosmic radiation and radiation background, are usually treated as the main factor which initiates the boiling of liquid and leads to the bending of isobars [7]. However, it is difficult to explain so strong an effect of gas saturation on the decrease in the stability of metastable solution in the initiation region while remaining within the framework of this model alone.

In the regions where the nucleation rate increases sharply, the magnitude of the derivative  $d\ln J/dT$  within the experimental error does not depend on concentration. At  $p = 1.171 \text{ MPa}$ , it is  $\sim 18$  and, at  $p = 1.667 \text{ MPa}$ , it reaches 21. This corresponds to the increase in the nucleation rate by approximately eight–nine orders of magnitude with a temperature rise by 1 K.



**Fig. 2.** The temperature dependence of the nucleation rate at a pressure of (a) 1.171 MPa and (b) 1.667 MPa and concentration of (1)  $c' = 0$ , (2) 0.08, (3) 0.14, and (4) 0.20 mol %. Dashed line indicates the results of calculation by the theory of homogeneous nucleation with  $\sigma = \sigma_\infty$  (oxygen), and dotted line indicates the same but with  $\sigma = \sigma(R_*)$  (oxygen and helium–oxygen solution).

### NUCLEATION THEORY

The theory of boiling of gasified nonvolatile liquids such as solutions of gas in liquid was treated by Deryagin and Prokhorov [9] and by Kuni *et al.* [10]. In these studies, the thermodynamic state of the nucleus was characterized by two variables, namely, the bubble volume  $v$  and the pressure of the gas component in this bubble,  $p''_1$ . The general case of boiling of a metastable solution is treated in [11], where, according to the Zel'dovich–Kramers scheme [12], the fluctuation growth of near-critical bubbles is presented as a diffusion process in the field of thermodynamic forces in the space of the variables such as the bubble volume  $v$  and the partial pressure of mixture components in the bubble  $p''_1$  and  $p''_2$ . The classical expression

$$J = C_v |\lambda_0| \frac{R_*^2}{v_*} \left( \frac{kT}{\sigma} \right)^{1/2} \exp - \frac{W_*}{kT} = C_v B \exp - \frac{W_*}{kT} \quad (1)$$

was derived for the steady-state nucleation rate. Here,  $C_v$  is the normalization constant of the equilibrium volume distribution function of nuclei;  $R_*$  and  $W_*$  denote the radius and work of formation of the critical bubble, respectively;  $\sigma$  is the surface tension of the bubble;  $\lambda_0$  is the decrement of the rise of an unstable variable (nucleus volume); and  $B$  is a kinetic factor. The dynamics of bubble growth are included mainly via the decrement  $\lambda_0$  for which a cubic equation was derived in [11]. In solving the dynamic problem, it was assumed that the motion of the molecules of the gas component in the solvent towards the bubble was diffusive; however, the exchange of molecules between the solution and bubble occurred only in a free-molecular mode. If two

components of absorptive–emissive interaction between the bubble and solution, namely, the diffusive delivery of substance to the bubble and the free-molecular exchange at the bubble boundary, are treated as independent processes occurring in parallel with each other, the rate of variation of the number of molecules of mixture components in the bubble will be defined by the expression

$$\dot{N}_1 = (\dot{N}_{1m}^{-1} + \dot{N}_{1D}^{-1})^{-1}, \quad \dot{N}_2 = \dot{N}_{2m}, \quad (2)$$

where

$$\dot{N}_{im} = \frac{\pi \beta v_{ti} R^2}{kT} (p''_{i*} - p''_i) \quad (3)$$

is the rate of molecular exchange;

$$\dot{N}_{1D} = 4\pi R \rho' D_g H (p''_{1*} - p''_1) \quad (4)$$

is the rate of diffusive delivery;  $\beta_i$  is the condensation number;  $v_{ti} = (8kT/\pi m_i)^{1/2}$  denotes the mean thermal velocity of motion of molecules of mixture components in the bubble;  $m_i$  is the molecular mass;  $\rho'$  is the density of the solution;  $D_g$  is the diffusion coefficient of the gas component in liquid; and  $H$  is Henry's law constant.

Much as this was done in [11], one can demonstrate that, with such treatment of interaction between the bubble and solution, the diffusion tensor of nuclei in the space of their essential variables will now be symmetric, and the decrement of the rise of the unstable vari-

able will be determined by solving the equation

$$\begin{aligned} \tilde{\lambda}^3 - \left[ \frac{3-b}{3b} + \frac{v}{b_1 v \omega_1 + 1} + \frac{1}{b_2 \omega_2} \right] \tilde{\lambda}^2 + \frac{1}{b_1 b_2} \\ \times \left[ \frac{b_1 v}{b_1 v \omega_1 + 1} + \frac{1}{\omega_2} + \frac{3-b_1}{3} \frac{1}{\omega_2} + \frac{3-b_2}{3} \frac{b_1 v}{b_1 v \omega_1 + 1} \right] (5) \\ \times \tilde{\lambda} + \frac{1}{3} \frac{v}{b_1 v \omega_1 + 1} \frac{1}{b_2 \omega_2} = 0, \end{aligned}$$

where

$$b = \frac{2\sigma}{p_*'' R_*}, \quad \omega_i = \frac{p_*'' R_*}{\beta_i v \eta}, \quad v = \frac{2D_g H \rho' \eta k T}{\sigma R_*},$$

and  $\eta$  is the viscosity of the solution.

If it is required that  $p_{2*}'' \rightarrow 0$ ,  $\beta_2 \rightarrow 0$ , and  $c' \neq 0$ , which corresponds to the boiling of gasified nonvolatile liquid, the cubic equation (5) reduces to quadratic. The diffusive delivery of substance to the bubble may be ignored if the characteristic time of diffusion is much less than the other time scales associated with the variation of pressure in the bubble. In this case,  $v \rightarrow \infty$ , and Eq. (5) yields the equation in [9] for determining  $\lambda_0$  in a viscous nonvolatile solution in which the concentration is uniform up to the separation surface of the bubble. If the free-molecular mode of evaporation of gas into the bubble is ignored, i.e.,  $\beta_1 \rightarrow 0$ , Eq. (5) changes to the equation in [10] and, simultaneously with Eq. (1), defines the nucleation rate in a nonvolatile viscous gasified liquid, when the transport of gas molecules to the bubble is limited by diffusion alone.

The calculation results demonstrate that, in all approximations, the value of the kinetic factor  $B$  in formula (1) depends very little on temperature, pressure, and concentration, compared with the exponential factor. Neglect of the volatility of the solvent and its viscosity leads to an increase in  $B$  compared with its value calculated from the general formula (5). Now, neglect of the diffusion mode of delivery of substance to the bubble likewise causes an increase in the value of  $B$ . In the region of spontaneous boiling of a helium-oxygen solution, the difference between the values of  $B$  calculated for different limiting cases, when the dynamics of bubble growth are limited by one or another factor, does not exceed one order of magnitude of  $B$ . This causes uncertainty in the temperature of limiting superheating of liquid of the order of 0.1 K. A similar uncertainty in the superheating temperature is introduced by the inaccuracy of the order of 3% in the work of formation of a nucleus.

## WORK OF FORMATION AND SURFACE TENSION OF CRITICAL BUBBLE

In Gibbs' method of separation surfaces, we have, for the work of formation of a critical nucleus [7],

$$W_* = \frac{16}{3} \frac{\pi \sigma^3}{(p_*'' - p')^2}. \quad (6)$$

The pressure in the nucleus  $p_*''$  is defined by the condition of its material (chemical) equilibrium with the surrounding metastable phase,

$$\mu_i(T, p_*'', c_*') = \mu_i(T, p', c'), \quad (7)$$

and the correlation between the surface tension  $\sigma$  and the radius of the tension surface of the bubble is given by Laplace's relation,

$$p_*'' - p' = 2\sigma/R_*. \quad (8)$$

Here,  $\mu_i$  is the chemical potential of the  $i$ th component.

A rigorous approach to the calculation of  $W_*$  calls for the knowledge of  $\sigma$  as the interface curvature function and of the equation of state describing the stable and metastable regions of the solution. The problem on finding  $\sigma(R_*)$  and on calculating  $W_*$  without introducing the concepts of separation surfaces may be solved if Gibbs' method is supplemented with van der Waals' method of gradient expansion [13]. According to the latter, the increment of a high thermodynamic potential during the formation of spherical nonuniformity in a binary system is given by the expression

$$\Delta\Omega\{\rho_1, \rho_2\} = 4\pi \int_0^\infty \left[ \Delta\omega + \sum_{i,j=1}^2 k_{ij} \frac{d\rho_i}{dr} \frac{d\rho_j}{dr} \right] r^2 dr, \quad (9)$$

where

$$\begin{aligned} \Delta\omega &= p' - p + \sum_{i=1}^2 [\mu_i(\rho_1, \rho_2) - \mu'_i] \rho_i \\ &= f(\rho_1, \rho_2) - f' - \sum_{i=1}^2 (\rho_i - \rho'_i) \mu'_i, \end{aligned}$$

$f$  is the density of free energy of a homogeneous system, and  $k_{ij}$  is the matrix of influence coefficients. A single prime indicates the initial value of a parameter in the liquid phase, and a parameter without a prime indicates the running local value.

From the conditions of stability of a two-phase two-component system follows

$$k_{11} k_{22} - k_{12}^2 > 0, \quad k_{11} > 0, \quad k_{22} > 0. \quad (10)$$

If

$$k_{12} = (k_{11} k_{22})^{1/2} \quad (11)$$

is assumed for the cross coefficient  $k_{12}$  [14], inequality (10) changes to an equality, which conforms to the indifferent equilibrium of the system relative to density gradients opposite in sign and defines the limiting per-

missible value of the coefficient  $k_{12}$ . In view of (11), expression (9) takes a simpler form,

$$\Omega\{\rho_1, \rho_2\} = 4\pi \int_0^\infty \left[ \Delta\omega + k_{22} \left( \frac{d\rho_\beta}{dr} \right)^2 \right] r^2 dr. \quad (12)$$

Here,  $\rho_\beta = (k_{11}/k_{22})^{1/2}\rho_1 + \rho_2$ . The distribution of density  $\rho_i$  ( $i = \beta, 1, 2$ ) in the critical bubble is found from the solution of a set of Euler equations for the functional (12), which includes one differential equation

$$\frac{d^2\rho_\beta}{dr^2} + \frac{2d\rho_\beta}{r dr} = \frac{\mu_2 - \mu'_2}{2k_{22}} \quad (13)$$

with the boundary conditions of  $\rho_\beta \rightarrow \rho'_\beta$  at  $r \rightarrow \infty$  and  $d\rho_\beta/dr \rightarrow 0$  at  $r \rightarrow 0$  and  $r \rightarrow \infty$  and one algebraic equation

$$\mu_1 - \mu'_1 = (k_{11}/k_{22})^{1/2}(\mu_2 - \mu'_2). \quad (14)$$

In so doing, the work of formation of a critical bubble is

$$W_* = \min \max \Delta\Omega\{\rho_1, \rho_2\}. \quad (15)$$

Expression (15) provides a way toward the calculation of  $W_*$  that is alternative to (6) and, simultaneously with (6)–(8), enables one to determine the correlation  $\sigma(R_*)$ . The solution of this problem implies the knowledge of the equation of state for binary solution and of the influence coefficients  $k_{ij}$ . The values of  $k_{ij}$  are functions of temperature and depend little on density [13, 14]. One can ignore the dependence of  $k_{ij}$  on  $\rho_i$  and determine the coefficient  $k_{22}$  for pure solvent by the data on surface tension at a plane interface,

$$\sigma_\infty = 2k_{22}^{1/2} \int_{\rho'_s}^{\rho''_s} (\Delta\omega)^{1/2} d\rho. \quad (16)$$

In so doing, the distribution of density  $\rho_\beta$  in the transition layer is found from the solution of the equation

$$k_{22} \left( \frac{d\rho_\beta}{dz} \right)^2 = \Delta\omega \quad (17)$$

with known boundary conditions.

The equation of state for the helium–oxygen system, describing both the stable and metastable regions, was derived within the one-liquid model of solution based on the unified equation of state for oxygen in [15]. Because the range of existence of the liquid phase for oxygen lies much higher than the critical temperature of helium, helium in this case may be treated as a

close-to-ideal gas. This enables one to use the equation of state for oxygen for describing the helium properties,

$$p/\rho RT = 1 + \zeta \sum_{i,j} b_{ij} \tilde{\rho}^i \tilde{T}^{-j}. \quad (18)$$

with the correction factor  $\zeta$  introduced into the latter equation.

Here,  $\tilde{\rho} = \rho/\rho_{c2}$ ;  $\tilde{T} = T/T_{c2}$ ;  $\rho_{c2}$  and  $T_{c2}$  denote the density and temperature at the critical point of oxygen, respectively; and  $R$  is the universal gas constant; the values of the coefficients  $b_{ij}$  are given in [15]. In pure oxygen,  $\zeta = 1$ ; at  $\zeta = 0.431$ , the equation of state (18) with the coefficients  $b_{ij}$  for oxygen provides the most optimal description of the  $p, \rho, T$  properties of helium in the range of reduced density  $0 < \tilde{\rho} < 1$  and temperature  $0.6 < \tilde{T} < 1$ .

In describing the helium–oxygen solution, three individual parameters of Eq. (18)  $T_c, \rho_c = 1/v_c$ , and  $\zeta$  are treated as functions of concentration,

$$T_c(c) = T_{c1}c^2 + 2\alpha_T T_{c12}c(1-c) + T_{c2}(1-c)^2, \quad (19)$$

$$v_c(c) = v_{c1}c^2 + 2\alpha_v v_{c12}c(1-c) + v_{c2}(1-c)^2, \quad (20)$$

$$\zeta(c) = \zeta_1 c^2 + 2\alpha_\zeta \zeta_{12} c(1-c) + (1-c)^2, \quad (21)$$

where the cross terms  $T_{c12}$ ,  $v_{c12}$ , and  $\zeta_{12}$  are given by the relations

$$T_{c12} = (T_{c1}T_{c2})^{1/2}, \quad (22)$$

$$v_{c12} = (v_{c1}^{1/3} + v_{c2}^{1/3})^3/8, \quad (23)$$

$$\zeta_{12} = (1 + \zeta_1)/2. \quad (24)$$

The free parameters of Eqs. (19)–(21)  $\alpha_T$ ,  $\alpha_v$ , and  $\alpha_\zeta$  may be determined by the saturated vapor pressure and by the composition of coexisting phases of the solution. However, the available literature data on  $p_s$ ,  $c'_s$ , and  $c''_s$  [4] proved to be insufficient for reliable reproduction of the phase diagram in the temperature region adjoining the critical point of the solvent; therefore, the data about the surface tension of solution [5] was used as additional information. This enabled us both to improve the reliability of description of the  $p, \rho, T, c$  parameters and to determine the influence coefficient of pure helium  $k_{11}$ . The calculations were performed by Eqs. (18)–(24) in [16, 17]. The data on the surface tension of pure oxygen were borrowed from [16]. The results of determining the free parameters of the unified equation of state for helium–oxygen solution are given in [17].

The distribution of the density of mixture components in a critical bubble, obtained by numerical integration of the set of equations (13) and (14), is given in Fig. 3. Unlike solutions with complete solubility of

components (of the Ar-Kr type), the density of the first (gas) component in the bubble is higher than in the solvent. The presence of a weak maximum on the density profile on the gas phase side points to excess adsorption of the gas component in the surface layer of the nucleus.

The tension surface radius  $R_*$  and the surface tension  $\sigma$  of the critical bubble are defined by the set of equations (6)–(8) and (15). For the radii  $R_{e,i}$  of equimolecular separation surfaces of the components, we have

$$R_{e,i} = \left( \frac{3n_i}{4\pi\Delta\rho_i} \right)^{1/3}, \quad \Delta\rho_i = \rho'_i - \rho''_i, \quad (25)$$

$$n_i = 4\pi \int_0^{\infty} |\rho_i - \rho'_i| r^2 dr.$$

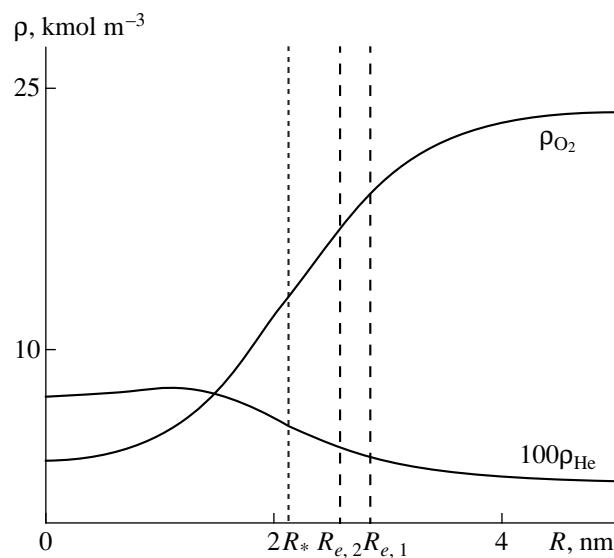
The behavior of the Tolman parameters of the components of binary solution ( $\delta_i = R_{e,i} - R_{*,i} = 1, 2$ ) is similar to that of the Tolman parameter  $\delta$  of pure substances: they increase monotonically with the curvature of the interface. In the region of large curvature radii (in the region of weak metastability), the relationship  $\delta_i(1/R_*)$  is linear. In the case of small radii of the tension surface (region of strong metastability), the Tolman parameters diverge as  $R_*^{1/3}$ . As distinct from  $\delta_1$  and  $\delta_2$ , the quantity  $\delta_{1(2)} = \delta_1 - \delta_2 = R_{e,1} - R_{e,2}$  demonstrates a weak dependence on both the curvature of the separation surface and the concentration.

Figure 4 gives the surface tension of critical bubbles of a helium-oxygen solution in the region of spontaneous boiling as a function of curvature of the tension surface. Minor additions of helium to liquid oxygen do not change the behavior of the dimensional dependence of surface tension of the solvent, while decreasing this tension monotonically. The inclusion of the dependence  $\sigma(R_*)$  in the work of critical nucleation causes a decrease in the height of the activation barrier and facilitates the boiling of the solution.

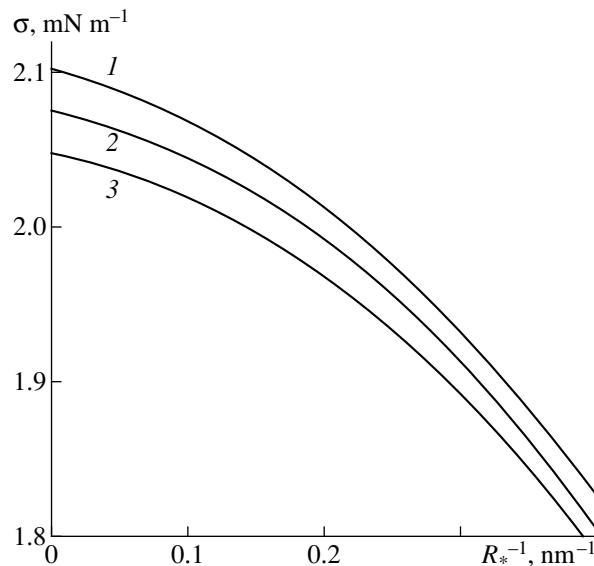
### COMPARISON OF THEORY AND EXPERIMENT

Solution (1) is valid after some incubation period of time  $t_l$  following which the nuclei, irrespective of their initial distribution, are generated with a regular frequency  $J$ . The time  $t_l$  may be estimated as the time of diffusive climbing of nuclei of the new phase over the critical region of the potential barrier by the unstable variable  $t_l = t_v = 1/\lambda_0$ . As was demonstrated in [18], for helium-oxygen solution in the region of parameters of state in which the experiments were performed, the time  $t_l \approx 10^{-8}$  s, this justifying the neglect of nonstationarity.

The exponential term is predominant in the expression for nucleation rate (1). The value of kinetic factor  $B$  depends little on temperature, pressure, and concen-



**Fig. 3.** The distribution of the density of mixture components in a critical bubble ( $T = 140$  K,  $c' = 0.1$  mol %,  $p = 1.0$  MPa).



**Fig. 4.** The surface tension of critical bubbles in a He-O<sub>2</sub> mixture at  $T = 140$  K and concentration of  $c' = (1) 0, (2) 0.1$ , and (3) 0.2 mol %.

tration. Because of the very strong dependence of the nucleation rate on the exponent, the differences in the estimates of the coefficient  $B$  are of little importance. The indeterminacy of the value of the kinetic factor  $B$  of one–two orders of magnitude leads to indeterminacy of 0.1–0.2 in the temperature of attainable superheating of liquid, which does not exceed the error of its experimental determination.

Another important aspect associated with the use of formula (1) is the value of the normalization constant of

**Table 1.** The temperature of attainable superheating of helium–oxygen solutions,  $J = 10^7 \text{ s}^{-1} \text{ m}^{-3}$ 

$c'$ , mol %	$T_s$ , K	$p_s$ , MPa	$T_{sh}$ , K		
			experiment	theory*	theory**
$p = 1.171 \text{ MPa}$					
0	122.40	2.570	138.17	138.43	137.96
0.08	118.96	2.640	137.79	138.07	137.58
0.14	114.55	2.686	137.43	137.80	137.28
0.20	—	2.732	137.06	137.52	136.99
$p = 1.667 \text{ MPa}$					
0	129.05	2.786	140.00	140.28	139.91
0.08	127.12	2.860	139.72	139.91	139.53
0.14	125.34	2.910	139.46	139.63	139.23
0.20	123.04	2.963	139.23	139.35	138.94

\* Calculations for  $\sigma = \sigma_\infty$  by the data of [5].

\*\* Calculations for  $\sigma = \sigma(R_*)$ , our results.

the equilibrium volume distribution function of nuclei,  $C_v$ . It is usually assumed that a nucleus may form on any molecule of the system; then,  $C_v = \rho' = \rho'_1 + \rho'_2$ , where  $\rho'_1$  and  $\rho'_2$  denote the number density of solvent and solute in the liquid phase, respectively. A more rigorous approach to the determination of  $B$  is given by Deryagin *et al.* [19], according to which  $C_v = v_* \rho'^2$ . The transition from the normalization constant  $C_v = \rho'$  to  $C_v = v_* \rho'^2$  results in a decrease in the temperature of attainable superheating of helium–oxygen solution by approximately 0.2–0.3 K. In what follows, in comparing theory and experiment, we use the normalization constant for the nucleus distribution function suggested by Deryagin *et al.* [19].

Table 1 gives data on the temperature of attainable superheating of helium–oxygen solutions, which correspond to the nucleation rate  $J = 10^7 \text{ s}^{-1} \text{ m}^{-3}$ . The experimental results are compared with the results of calculation of  $T_n$  by the theory of homogeneous nucleation in a macroscopic approximation ( $\sigma = \sigma_\infty$ ) and with due regard for the dependence of the bubble surface tension on the curvature of its separation surface ( $\sigma = \sigma(R_*)$ ). The kinetic factor  $B$  was determined by the decrement found from the solution of Eq. (5). Figure 2 gives the temperature dependence of  $J$  in view of  $\sigma(R_*)$ , calculated by the theory of homogeneous nucleation and, for pure oxygen, in a macroscopic approximation as well. The data of Tables 1 and 2 demonstrate good agreement between experiment and theory, when the latter includes the dimensional effect. The divergence between the theoretical and experimental values of the temperature of attainable superheating is within the limits of the experimental error and the accuracy of the thermal parameters appearing in (1). This agreement is an indirect vindication of the theoretical assumption of

the equilibrium composition of vapor–gas mixture in the critical nucleus.

The typical parameters of critical bubbles under experimental conditions are given in Table 2. With a temperature  $T = 138 \text{ K}$  and pressure  $p = 1.171 \text{ MPa}$ , the radius of critical bubble in superheated pure oxygen  $R_* = 3.83 \text{ nm}$  and the number of molecules in the bubble  $n_*'' \approx 485$ . The dissolution of 0.2 mol % helium in the bubble increases the critical bubble size to  $R_* \approx 4.26 \text{ nm}$ . In so doing, the concentration of helium in the bubble  $c_*'' = 6.8 \text{ mol } \%$ , and the number of molecules  $n_*'' \approx 640$ , and the bubble is in fact free of helium atoms:  $n_{1*}'' \approx 50$ . Before the formation of the bubble, its volume was occupied by  $n_2' \approx 5674$  molecules of oxygen and  $n_1' \approx 13$  atoms of helium. In order to attain an equilibrium composition, the lacking  $\approx 37$  atoms may be delivered to the growing bubble in the process of chaotic thermal motion. Therefore, the process of nucleation in a gas-saturated solution at a temperature close to the temperature of attainable superheating of solvent and to its critical point differs little from the process of nucleation in a superheated pure liquid. A decrease in the temperature of superheating of liquid as the gas component is dissolved in the liquid is primarily associated with the shift of the line of equilibrium coexistence of phases and, to a smaller extent, with the variation in surface tension.

The situation changes drastically if the nucleation occurs at low temperatures. For example, at a temperature  $T = 100 \text{ K}$  and pressure  $p = 1.171 \text{ MPa}$ , when the concentration of helium in oxygen is  $c' = 0.03 \text{ mol } \%$  and the solution is supersaturated so that the Gibbs number  $G = W_*/kT = 80$ , i.e., close to that which we had in experiments in the boiling of helium–oxygen

**Table 2.** The typical parameters of critical bubbles of pure oxygen and of helium–oxygen solutions at a pressure  $p = 1.171$  MPa in the vicinity of the boundary of spontaneous boiling

Parameter	$c'$ , mol %		
	0	0.1	0.2
$T$ , K	138	137	136
$p_s$ , MPa	2.550	2.583	2.626
$W_*/kT$ , Eq. (6)	89.78	107.09	124.80
$W_*/kT$ , Eq. (15)	74.78	91.39	108.28
$\log J$ , Eqs. (1), (5), and (6)	1.07	-6.89	-14.83
$\log J$ , Eqs. (1), (5), and (15)	7.55	-0.07	-7.65
$\sigma_\infty$ , mN/m	2.47	2.63	2.79
$\delta_{\infty,1}$ , nm	—	0.289	0.276
$\delta_{\infty,2}$ , nm	0.0363	0.0367	0.0373
$R_*$ , nm	3.828	4.066	4.262
$\sigma(R_*)$ , mN/m	2.32	2.50	2.67
$n''_*$	485	566	640
$n''_{1*}$	—	22	50
$\delta_1$ , nm	—	0.429	0.403
$\delta_2$ , nm	0.209	0.188	0.172
$c''_*$ , mol %	0	3.25	6.80

solutions at high temperatures, the critical bubble radius will be  $R_* \approx 1.7$  nm and the number of helium molecules in the bubble  $n''_* \approx 146$ , with the number of oxygen molecules  $n''_{1*} \approx 3$ . Prior to nucleation, approximately 12 atoms of helium were present in a volume of critical size. For an equilibrium to set in, the gas must diffuse to a distance of approximately 2.5 times the bubble radius. In this case, the characteristic time of diffusion is  $\tau_D = (2.5R_*)^2 D_g^{-1} \approx 2 \times 10^{-8}$  s, which is comparable with the time of relaxation to steady-state size distribution of nuclei. In addition, a stronger dependence of the surface tension of critical bubbles is possible in this case, which differs both quantitatively and qualitatively from that revealed at high temperatures (see Fig. 4). Therefore, more detailed theoretical and experimental studies are required for revealing the reasons for the discrepancy between the theory of homogeneous nucleation and experiment in gas-saturated solutions at low temperatures [20, 21].

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